



Simple model to study heterogeneous electrocatalysts



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HIGHLIGHTS

- Simple DFT-based methodology for studying morphologically heterogeneous catalysts.
- Model has good correlation with previous simulations and experimental data.
- Adsorption on “valleys” or cavities with both Pt and Pb atoms involved.

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ABSTRACT

New electrocatalyst materials have been proposed to increase the performance of fuel cells. Experimental studies show that Pt and Pb metallic and oxide materials are quite efficient in the oxidation of alcohols and small organic molecules such as formic acid in advanced fuel cells. This work proposes a model for studying morphologically heterogeneous catalysts through quantum chemistry methods such as density functional calculations. For testing the model, we have experimentally studied the adsorption of small organic molecules, namely formic acid and methanol, on Pt and Pb electrodes. All methodologies we have tested can be employed for this kind of study, but M06 functional results correlate best with previous simulations of homogeneous catalysts and with experimental data obtained for homogeneous and heterogeneous electrodes. Our model indicates that the presence of a Pt–Pb interface is responsible for higher adsorption energies of these molecules, most likely due to the orientation of the organic molecules that should facilitate the oxidation process.

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1. Introduction

The search for new energetic sources is fundamental to the near future of society; in this context, fuel cells are being widely studied. Fuel cells are devices with the ability of turning chemical energy into electric energy using electrocatalysts.

Studies by Suffredini et al. [1–5] for heterogeneous catalysts based on Pt, Pb, PbO_x and other metallic oxides have shown excellent performance for formic acid oxidation. The authors proposed that platinum poisoning can be avoided by the presence of lead and its oxides, which might curb the adsorption of some undesired intermediates in the reaction, such as acetic acid and acetaldehyde. These type of electrodes were synthesised by the sol–gel method, using acetates, carboxylates, acetylacetonates or metal alkoxides, among other salts. The electrodes obtained using the synthetic route presented in Ref. [5] are composed of distinct

phases of Pt and Pb and nanometric islands of Pt, which are heterogeneously dispersed on the carbon support. Some Pb particles are spread over the support, as shown in microscopy studies [5].

Computational simulations have been extensively applied in catalyst studies, including reactions related to fuel cells [6–17]. These simulations, however, are based on the periodic properties of morphological homogeneous electrodes. In our previous work [5], in addition to experimental results, we presented a simple method to investigate the behaviour of heterogeneous electrodes and their adsorption sites. In the present study, we validate the chosen computational methodology and extend the calculations to study methanol adsorption onto heterogeneous catalysts.

2. Computational details

Two main approaches are usually employed for *ab initio* simulations of adsorption processes: plane wave periodic techniques or cluster calculations. Both employ crystal parameters obtained for solids whose atoms are homogeneously distributed. Defects are

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introduced by the addition, removal or replacement of an atom of the crystal lattice.

As extensively discussed in previous publications [5,18], electrodes synthesised by sol–gel methodology present heterogeneous distributions of atoms what showed to improve their catalytic activity. The enhancement in the catalytic activity is attributed to the presence of active sites consisting of defects and/or interphases regions. Aiming to find geometries and composition for active sites, we built a very small model of the system, with metallic atoms (Pt and Pb) bonded to a carbon chain, and performed full geometry optimisations without symmetry restrictions with and without fuel molecule. Since our electrode model is a kind of molecule rather than a cluster, we employed quantum chemistry methods of simulation, namely gaussian-based DFT.

The electrode model employed in this work was inspired by the Dipped Adcluster Model [14,16,17], consisting of only four metallic atoms in different proportions of Pt and Pb. Thereby, cluster and adcluster geometry were fully optimised, with the only restriction imposed by the presence of a saturated carbon chain (with 7 carbon atoms and 12 hydrogen atoms) over the metallic atoms to induce them together. By this procedure, we intend to obtain optimal sites for adsorption.

We have performed a methodological study using the functionals M05 [19], M06 [20], M05-2X [21], B3LYP [22–24] and the LANL2DZ pseudopotential basis set [25–27]. The convergence criterion for the electronic self-consistent iterations was 1×10^{-8} a.u. The results obtained were compared to the interaction energy obtained in previous works [7,11,28] for the adsorption of formic acid on a homogeneous platinum surface.

We subsequently investigated the adsorption of formic acid and methanol on electrodes containing platinum and lead. We studied various electrode compositions, varying the relative atomic positions.

The inputs related to the interaction between clusters and fuels were chosen such that the distance between the adsorbate and the metal, composing the adcluster, was constant. However, the relative positions of the organic molecules were different, identified as A, B, C and D (as shown in Figs. 2 and 4). Frequencies were calculated to guarantee a minimum in the potential energy surface. Atomic charges derived from electrostatic charges (ESP) were obtained using the ChelpG scheme [29]. All calculations were carried out with the Gaussian 09 package [30].

3. Results and discussion

3.1. Cluster characterisation

The geometry of isolated adsorbate systems, formic acid and methanol, and catalysts, was first optimised using M05-2X, M05, M06 and B3LYP functionals with the LANL2DZ basis set (Table 1).

From these results, we can compare electrodes with the same number of electrons. When just one different atom is present (*b* and *c* or *h* and *i*), the cluster for which this atom is on the border (*b* and *i*) is generally more stable (except for the M05 functional). For the 2:2 Pt/Pb proportion (clusters *d*, *e*, *f* and *g*), the results for all functionals are consistent; the most stable cluster is that with Pb in the borders and 2 Pt in the middle (cluster *f*), followed by cluster *g*, in which Pt and Pb are intercalated, cluster *d*, with Pt in the borders, and cluster *e*, with two separated domains.

Fig. 1 presents the final conformations of the electrodes obtained with M06. In each electrode, there have been modifications in relation to the input structure, but all functionals predict similar structures. Distances between Pt atoms are approximately 2.6 Å and between Pb atoms 3.2 Å, smaller than the distances observed in crystal structure of the pure metal (respectively, 2.8 Å and 3.5 Å).

Pt–Pb distances range from 2.6 to 2.8 Å. The more stable structures with only one different atom, clusters *b* and *i*, have a zigzag structure, while clusters *c* and *h* are in arc form. For 2:2 clusters, the stability order, $f > g > d > e$, also follows the same geometric criteria, for which cluster *g* is in arc form and *e* is almost linear. For cluster *d*, there is a greater separation between Pb atoms.

Our previous works [5,18] demonstrated that these heterogeneous catalysts present different phases, with characteristics of both pure metal and alloy. In the present work, the electrode is represented as small clusters, which do not allows us to use band theory but enables us to compare changes in the electronic properties of electrodes by evaluating frontier molecular orbitals. In Table 2, the energies of frontier orbitals, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), as well as the difference between them (gap energy), are listed. The data were obtained with the M06 functional. DFT generally underestimates gap values [31]; however, qualitative comparisons between conformations can indicate general trends.

The electrode composed of pure lead presents a small gap value as do structures with a higher proportion of this atom (3:1). The cluster Pt–Pt–Pb–Pb has a quite low gap value. The other structures have behaviour closer to the pure Pt electrode but with higher values.

As the aim of this work is to assess the response of the catalysts to the oxidation of organic molecules, we have analysed the LUMO energies for several compositions. The pure clusters, formed by only one kind of element, have a very low LUMO energy that indicates the facility to receive electrons. The LUMO energy of Pt–Pt–Pb–Pb is slightly more negative than the same for a pure cluster of platinum and 0.01 a.u. (approximately 0.27 eV) lower than that of a pure cluster of lead.

After these initial calculations, we began to study the interaction between fuel molecules and clusters, thus obtaining the adclusters presented in the following sections.

3.2. Formic acid

In the previous work [5], we have proposed some models to study formic acid electrooxidation, but the main focus was experimental results. Here, we present the theoretical methodology and models employed in a more detailed study of this system. Initial adcluster conformations (inputs) with formic acid are shown in Fig. 2. The intramolecular hydrogen bond of formic acid was avoided, as our aim is confirming the difference between both oxygen atoms. This system was fully optimised.

Based on total energies ($E_{\text{adcluster}}$) (Fig. S11, Supplementary information), obtained after optimising adcluster geometry (including all possible combinations of Pt and Pb and also considering every possible initial position for formic acid), we have calculated adsorption energies (E_{ads}) by the following equation:

$$E_{\text{ads}} = E_{\text{adcluster}} - E_{\text{cluster}} - E_{\text{fuel}}.$$

As noted previously [5], our calculations with the M06 functional, even with a simplistic approach, were able to reproduce qualitatively well the results of plane wave calculations for formic acid adsorption on a Pt electrode [7,11].

As a general bias, we can observe that the adsorption energy of formic acid onto different clusters is about -0.3 to -0.4 eV, as predicted by all functionals (Fig. S11 in Supplementary information). We can compare the M06 functional with its predecessors M05 and M05-2X (parameterised to weak interactions and non-metallic systems) and B3LYP, widely used among chemists. Our model provided the following mean values for the

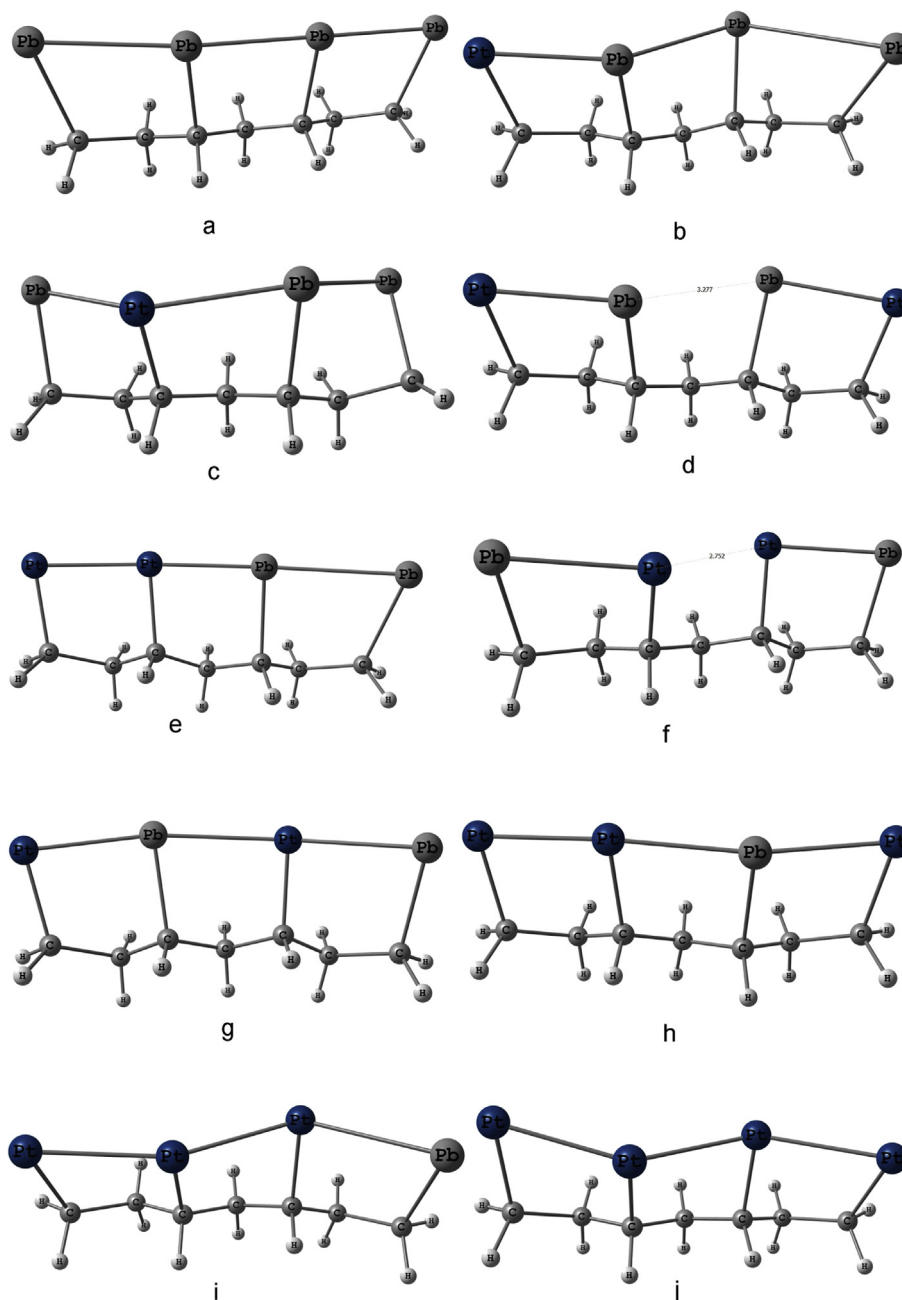


Fig. 1. Final conformations for the electrodes named in Table 1.

adsorption energy of formic acid on a pure platinum electrode: M05-2X: 0.50 eV, M05: 0.25 eV, M06: 0.37 eV and B3LYP: 0.22 eV, excluding the two saddle points of B3LYP conformations in this average.

The interaction energies predicted with functional M05-2X are always higher in magnitude than those obtained with other functionals, most likely because this functional includes weak forces of interaction.

For some clusters, especially Pt–Pb–Pb–Pb, Pb–Pt–Pb–Pb and Pt–Pt–Pb–Pb, there are more pronounced effects, sometimes predicted in different ways by different functionals. For Pb–Pt–Pb–Pb, M05 and M05-2X provide very different energies from the M06 and B3LYP tendencies.

Fig. 3 presents selected adcluster adsorption energies. The addition of Pb atoms has a notable effect only when Pt and Pb

atoms (2:2) are gathered; Pt–Pt–Pb–Pb revealed a different behaviour with more intense adsorption energies. The addition of only one Pb atom does not modify the adsorption energy, regardless of its position. Also, the cluster in which there are two Pt and two Pb atoms arranged alternatively have similar energies as the other configurations. Formic acid has in its composition two oxygen atoms, one ketonic and another enolic. If adsorption occurs through oxygen atom, the process releases more energy. As can be seen from Table 3, adsorption energies have straight correlation with variations on charges (Δq) of the components of adcluster, particularly with changes in the atomic charge of adsorbed oxygen: as greater is Δq on oxygen atom, greater (in absolute values) is the adsorption energy. Charge transfer is more effective for Pt–Pt–Pb–Pb composition than for electrode model with metallic atoms intercalated.

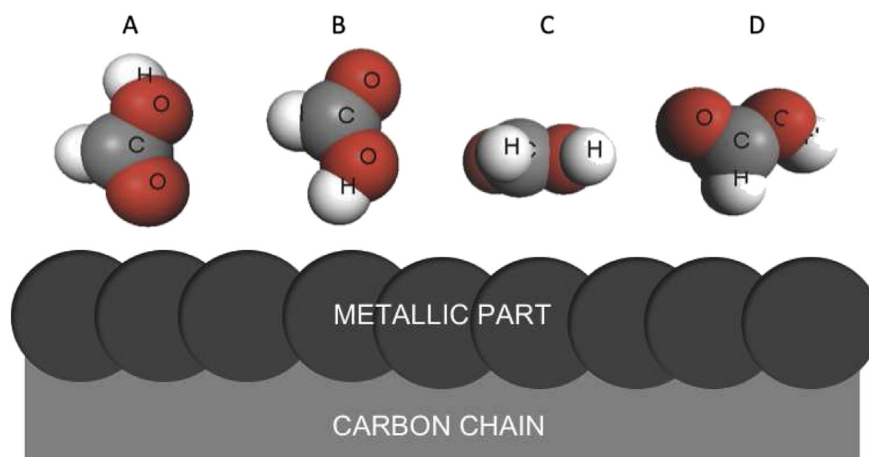


Fig. 2. Relative initial positions of formic acid.

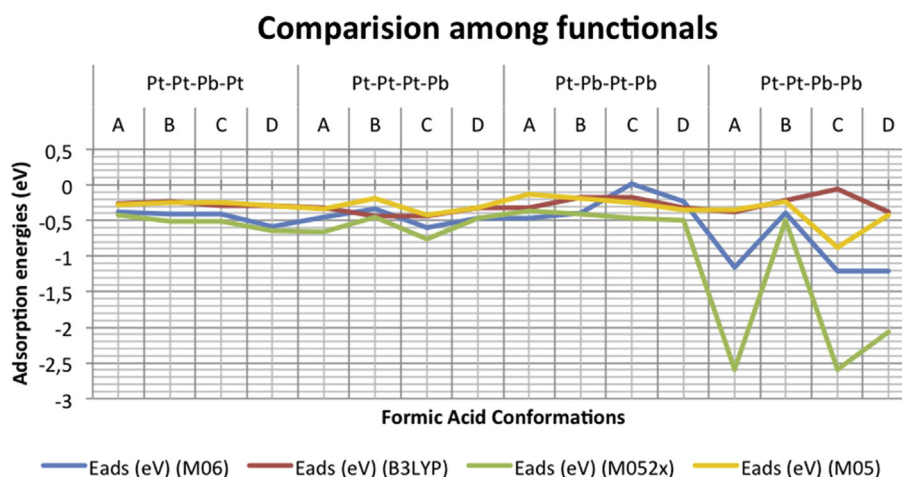


Fig. 3. Comparison among adsorption energies for formic acid on clusters obtained with the four functionals: M06, B3LYP, M05 and M05-2X.

B3LYP calculations for structure C for adsorption on Pt–Pt–Pb–Pb provided quite different adsorption energy from the general behaviour predicted by the other functionals because B3LYP discovered a very different geometry than that provided by the other functionals. We were not able to find a minimum in the potential energy surface with this methodology, for which we found one imaginary frequency (Table S12).

As a general bias, we conclude that the fuel formic acid prefers sites featuring lead (Pb) and platinum (Pt) islands because the best adsorption occurs at the interface of the two metals. Moreover, the fuel prefers sites where there are “holes” in the electrode, i.e., valleys or areas in which the fuel can be located between Pb and Pt, reinforcing that the importance of morphologically heterogeneous electrodes, as we have noted in previous works [5,18].

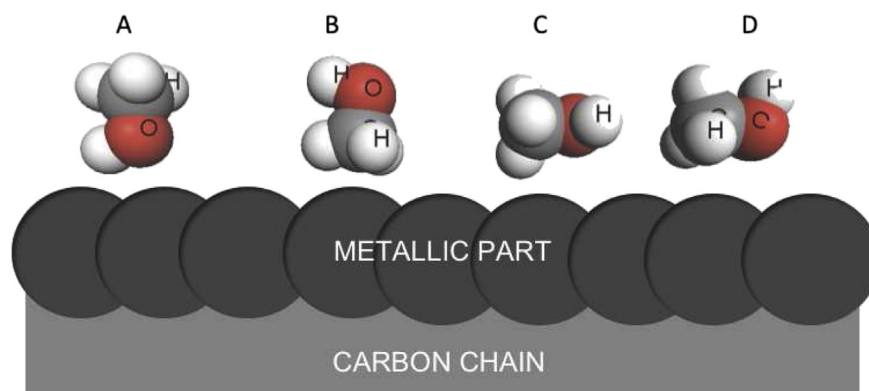


Fig. 4. Relative initial positions of methanol.

Table 1

Total electronic energies (in a.u.) of model electrodes (metallic atoms bonded to a carbon chain) calculated with four different functionals and the LanL2DZ basis set.

	Metallic composition	M05-2X	M05	M06	B3LYP
a	Pb–Pb–Pb–Pb	–287.6663	–287.4962	–287.5271	–287.7697
b	Pt–Pb–Pb–Pb	–403.2774	–403.1103	–403.2059	–403.4826
c	Pb–Pt–Pb–Pb	–403.1476	–402.9824	–403.2139	–403.4890
d	Pt–Pb–Pb–Pt	–518.8809	–518.7301	–518.8898	–519.2055
e	Pt–Pt–Pb–Pb	–518.8482	–518.7054	–518.8676	–519.1807
f	Pb–Pt–Pt–Pb	–518.90630	–518.74891	–518.91739	–519.22972
g	Pt–Pb–Pt–Pb	–518.89563	–518.74244	–518.90700	–519.21982
h	Pt–Pt–Pb–Pt	–634.45432	–634.32411	–634.54823	–634.89493
i	Pt–Pt–Pt–Pb	–634.45829	–634.32399	–634.55215	–634.89768
j	Pt–Pt–Pt–Pt	–750.00581	–749.89635	–750.18342	–750.56634

Table 2

Energies of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) orbitals (a.u.), and the difference between them ($\text{Gap}_{\text{LUMO-HOMO}}$), obtained with M06/LanL2DZ methodology.

	Metallic composition	E_{HOMO}	E_{LUMO}	$\text{Gap}_{\text{LUMO-HOMO}}$
	Pb–Pb–Pb–Pb	–0.16208	–0.11387	0.04821
	Pt–Pb–Pb–Pb	–0.17485	–0.1052	0.06965
	Pb–Pt–Pb–Pb	–0.15476	–0.09599	0.05877
	Pt–Pb–Pb–Pt	–0.20109	–0.10019	0.10090
	Pt–Pt–Pb–Pb	–0.17936	–0.12477	0.05459
	Pb–Pt–Pt–Pb	–0.18246	–0.08575	0.09671
	Pt–Pb–Pt–Pb	–0.18796	–0.09767	0.09029
	Pt–Pt–Pb–Pt	–0.19905	–0.10845	0.09060
	Pt–Pt–Pt–Pb	–0.18965	–0.10904	0.08061
	Pt–Pt–Pt–Pt	–0.20554	–0.12442	0.08112

3.3. Methanol

We have carried out similar calculations to study the adsorption of methanol, for which experimental data show that heterogeneous surfaces play relevant role [32]. Methanol molecule was also inserted next to clusters in pre-defined positions, A, B, C and D (Fig. 4).

From these initial configurations, we have obtained one structure as a minimum in the potential energy surface for each functional (with some exceptions, especially for the M05-2X and M05 functionals, for which many structures presented imaginary frequencies). Electronic energies can be found in Table S13, and the respective adsorption energies (differences between the total electronic energies of adclusters and isolated species) are shown in Figure S12 in Supplementary information.

For the reference material, a pure platinum electrode, the experimental adsorption energy for methanol is approximately 0.49 eV [33], while simulations suggested 0.39 eV [34] and 0.53 eV [35], both obtained with the slab model, and 0.51 eV with the DAM approach [6]. Our model provided greater adsorption energies for

all methodologies, with the following mean adsorption energies of methanol on a pure platinum electrode: M05-2X, 0.95 eV; M05, 0.62 eV; M06, 0.72 eV and B3LYP, 0.66 eV, excluding saddle points in this average. Again, M06 predicted values that are intermediate to the M05 and M05-2X values, and B3LYP predicted comparable values to the M05 data.

Figs. 5 and 6 present the adclusters obtained with M06 and B3LYP functionals for B and C initial conformations of methanol and an electrode formed only by platinum atoms. The adcluster obtained for B conformation with B3LYP is a saddle point (presents one imaginary frequency) and not a minimum in the potential energy surface. B and C conformations have been chosen once the determined values of adsorption energy correspond to the highest and lowest values for Pt-only electrodes. Analysing those structures, we can observe that the lowest values (greater adsorption energy, conformation C) are reached when the oxygen atom of the methanol molecule interacts with the cluster indicating a higher preference for this conformation. In contrast, the value obtained when the carbon of the methanol molecule interacts (Fig. 5, conformation B) with the cluster is lower in module and comparable to the experimental value.

Neurock et al. [11] found two pathways for the oxidation of methanol: the direct pathway, in which the C–H bond is activated and requires only 1 to 2 Pt atoms, and the indirect pathway, in which the O–H bond is activated and involves 3 to 4 Pt atoms. Our M06 simulations agree with these results (Figs. 5 and 6). Particularly, in Fig. 6, we find that the electrode folds in the direction of the fuel.

Fig. 7 compares adsorption energies obtained with the four functionals employed in this study for selected clusters. Generally, these energies are higher (in module) than those achieved for formic acid. In addition, the values are uniform for all clusters proposed, varying from –1.36 to –0.10 eV (in the case of formic acid, the range changes from –2.5 to 0.1 eV, Figure S13).

B3LYP and M05 have relevant agreement within the final results, especially for clusters with smaller quantities of Pb. Yet for those clusters, the contributions from weak interactions introduced by the M05-2X functional makes the energies slightly more negative when compared to the other functionals. M06, which embodies an improvement to the M05 family, produces intermediate values among all functionals, as mentioned above. The energies fluctuate more when there is a higher concentration of Pb atoms. This oscillation may exist due to structural changes.

The results obtained for M06 functional seem to better correlate experimental results. This is probably due to the fact that this functional has been optimized for metals and weak interactions [21,36].

Fig. 8 presents the output conformations using M06 for cases of high and low energies in the same group of clusters and all structures for the Pt–Pt–Pb–Pb cluster.

Table 3

Atomic and group charges^a (q) for selected adclusters of formic acid and methanol obtained with M06/LanL2DZ methodology.

Fuel	Metallic composition (conformation)		q (groups)		Δq (oxygen atoms) ^b		E_{ads} (eV)	Adsorbed atom
			Adsorbed fuel	Metallic part	Ketonic	Enolic		
Formic acid	Pt–Pb–Pt–Pb	A	–0.011	–0.027	0.121	0.430	–0.472	O _{enolic} –Pb
		C	–0.070	0.047	–0.006	0.102	0.008	H–Pt/H–Pb
	Pt–Pt–Pb–Pb	B	0.081	–0.099	0.080	–0.094	–0.394	O _{ketonic} –Pt
		D	–0.009	–0.224	0.182	0.152	–1.209	O _{ketonic} –Pb O _{enolic} –Pt
Methanol	Pt–Pb–Pt–Pb	B	0.021	–0.054		0.048	–0.330	OH–Pt
		C	–0.016	0.020		0.245	–1.366	O–Pt
	Pt–Pt–Pb–Pb	A	0.237	–0.213		0.384	–1.108	O–2Pb
		C	–0.009	–0.175		–0.023	–0.427	OH–Pt

^a Charges derived from electrostatic surface potential (ESP) using ChelpG scheme.

^b Difference in relation to the isolated fuel molecule (Table S14).

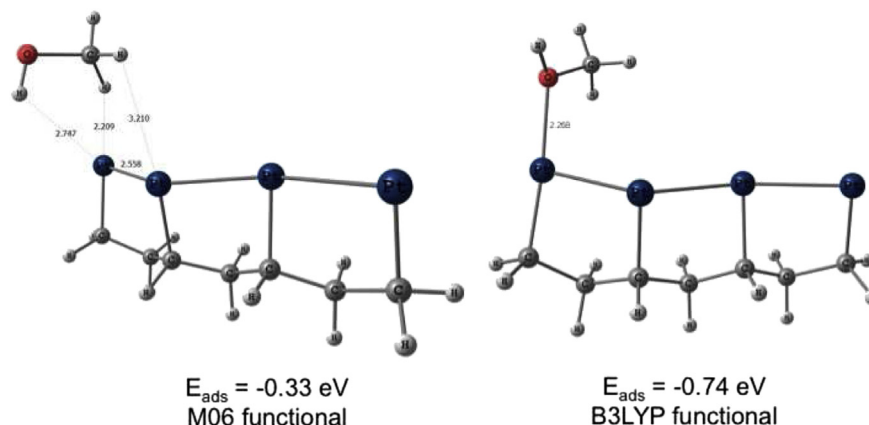


Fig. 5. Methanol adsorption onto a platinum cluster obtained with two different functionals for initial conformation B.

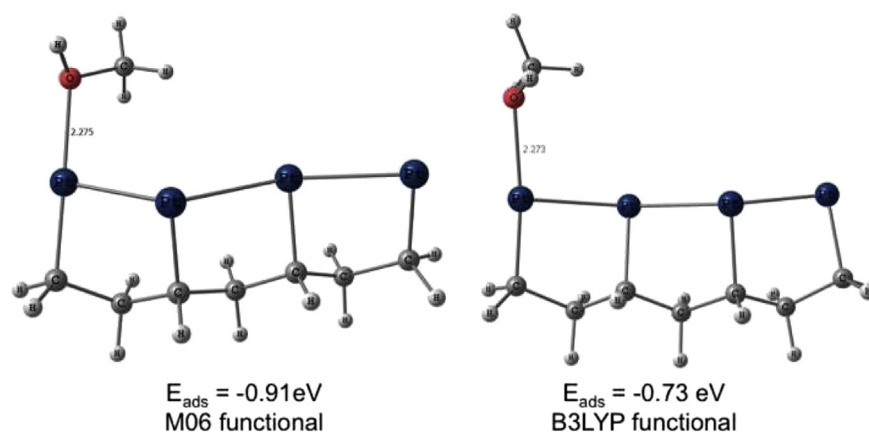


Fig. 6. Methanol adsorption onto a platinum cluster obtained with two different functionals for initial conformation C.

From the presented results, there is a preference of methanol for lead sites. In the first group, it is possible to observe that most negative energies result from the greater proximity of fuel oxygen atoms with lead atoms, and the cluster geometries remain very similar to those of the initial structures. When the proportion of lead is raised, greater interaction energies are reached (in module) if the cluster geometry is modified significantly from the initial one.

In the case of 2 atoms of platinum and 2 interchangeable lead atoms, the oxygen from the methanol bonds to the platinum; when there are 2 atoms of lead side-by-side, the oxygen has a preference for those atoms. As observed for formic acid adsorption, stronger adsorptions correspond to more effective charge transfers (Table 3). This effect is even more pronounced for methanol because it presents a single oxygen atom.

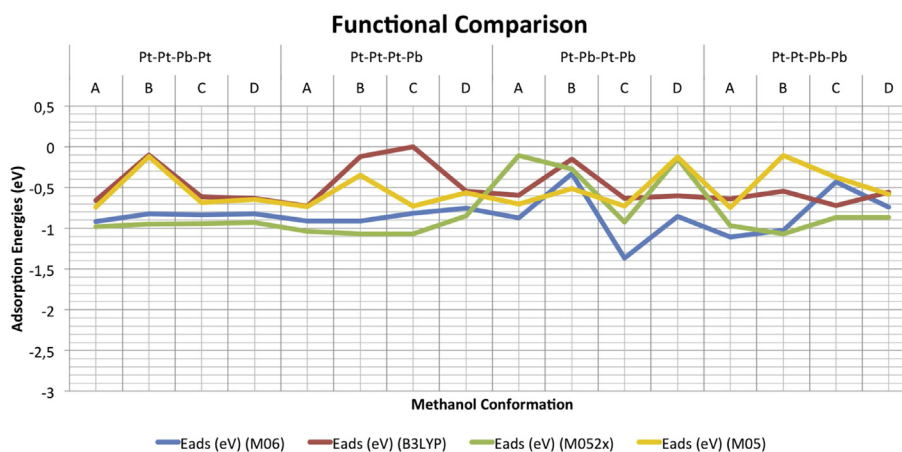


Fig. 7. Comparison among adsorption energies for methanol on clusters obtained with the four functionals: M06, B3LYP, M05 and M05-2X.

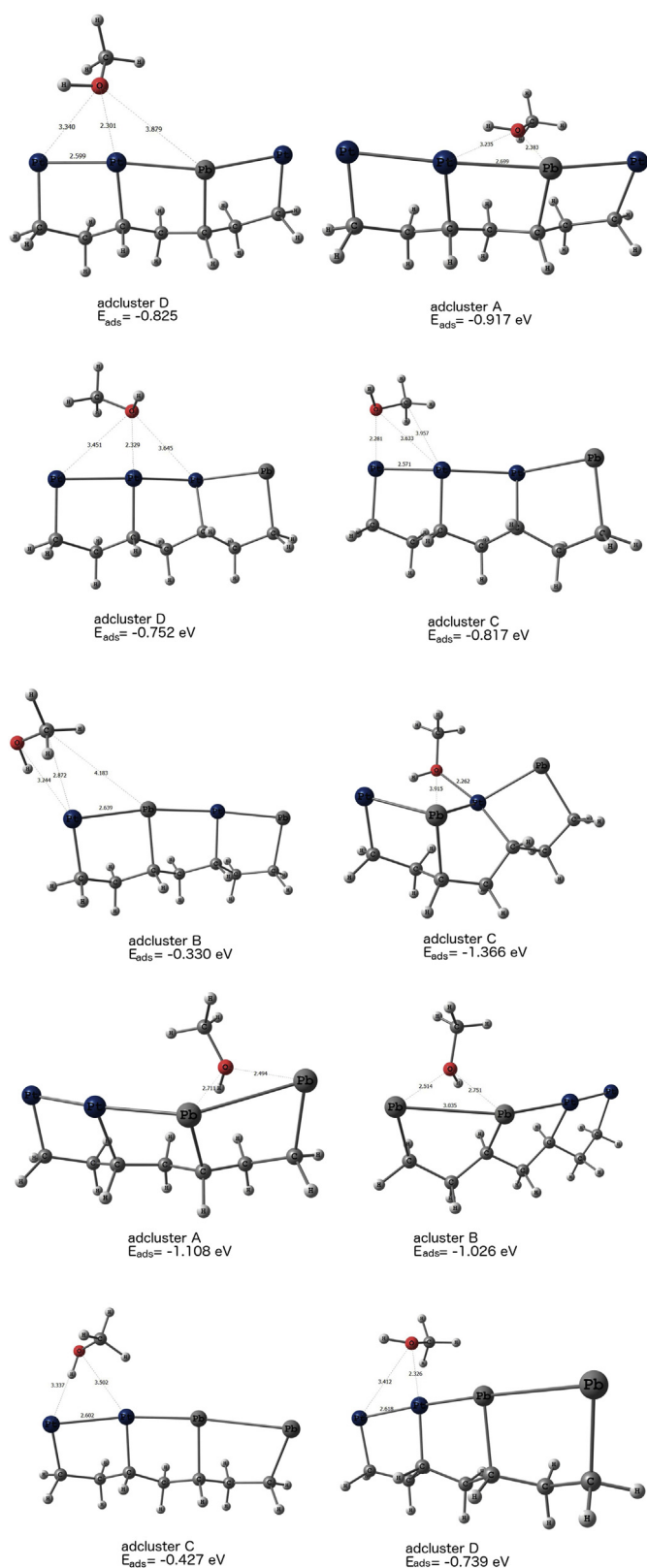


Fig. 8. Selected structures and respective adsorption energies for methanol on electrodes with different metallic composition, as obtained with M06/LanL2DZ methodology.

4. Conclusions

In this work, we propose a model to study morphological heterogeneous electrodes composed by Pt and Pb atoms. From these studies, we have determined the main electrode domains that efficiently promote oxidation of small organic molecules.

The model reproduces adsorption conformations and energies already presented in the literature (obtained with the well-established method of plane waves) for adsorption of formic acid and methanol on homogeneous platinum catalysts, with the additional advantage of being applicable to heterogeneous solids.

According to the deformations observed in the electrodes, after the system finds the minimum in its potential energy surface, the fuel prefers sites such as valleys or cavities in the electrode, with groups of two species of metallic atoms involved, binding more strongly to lead and possibly allowing oxidation to occur without poisoning platinum. Furthermore, analysis of the frontier molecular orbital energies indicates that the Pt–Pt–Pb–Pb cluster has a gap comparable to the “pure” clusters and greater ability to accept electrons than other proposed clusters. Atomic charges corroborate the tendency of adsorption on lead by more efficient charge transfer.

Some hybrid functionals were tested and produced quite similar results. The results obtained for the M06 functional better correlate experimental results, most likely because this functional has been optimised for metals and weak interactions.

The main limitation of the model is related to the absence of bulk metal atoms. However, the proposed model is very useful because it allows for initial exploration of the target system, proposing conformations for active sites with relatively low computational costs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.09.099>.

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